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Recent Developments in Wet Strength Chemistry Targeting High Performance and Ambitious Environmental Goals

Abstract
Highly reactive polyamido-amine-epichlorohydrin resins are the products of choice to produce paper grades with high wet strength. Due to the crosslinking chemistry (of epichlorohydrin) this group of chemical additives is associated with AOX-emissions in the effluent and critical chlorinated monomers like DCP (Dichloropropanol) and MCPD (Monochloropropanediol). At lot of research has been carried out to reduce the content of those by-products significantly, not at least to fulfill increasingly regulatory requirements. This paper shows the history and actual status of those regulations in Germany, and accordingly, the development of market products with respect to the requirements on the product itself, but on the mill effluent situation as well. Today's products (3rd generation) do offer DCP contents of some ppm compared to values up to 1 % in historical standard products (1st generation).
At the same time the suppliers managed to maintain or even improve the performance of the products. Compared to a couple of years ago, the papermaker nowadays has a choice of products with outstanding cost/efficiency meeting all environmental regulations.
Figures from some case studies in different applications are given to illustrate this development.

1. Introduction

Wet strength is the mechanical strength of paper remaining after complete soaking in water. Wet Strength Agents (WSA) are synthetic resins intended to reinforce mechanical properties of wet paper. These resins are applied in various paper grades such as: Tissue, Packaging Papers (Liquid Packaging Board), Specialty Papers (bank note paper, filter paper, abrasive paper, label paper, decorative laminating paper, wall paper etc.).
Wet strength resins are available on different chemical basis. This presentation deals with epichlorohydrin resins, which are most suitable for neutral and alkaline paper manufacturing

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This paper was presented at ChinaPaper, Beijing, September 2009

Beside other chemistries epichlorohydrin resins cover more than 90 % of the WSA market nowadays. Alternative products based on melamine or urea are declining due to their formaldehyde content and are still used in some specialty papers, only. This paper deals with the chemistry of the epichlorohydrin resins, their environmental aspects and related application case studies.

Dosage	Application field
< 1 %	retention anionic trash control creping agent
1 - 2 %	printing runnability and pick resistance (newsprint, carton and corrugating)
2 - 8 %	normal wet strength (tissue and towel, liquid packaging board, food packaging, carton and corrugating)
> 8 %	high wet strength (laminates, security paper, label papers)

Fig. 1: Application field and dosage of epichlorohydrine resins

Fig. 1 gives an overview of the major application fields and the product dosage. Almost no wet strength will be achieved with dosages (of product as it is) less than 1 % (based on dry fibers). Still, a retention support will be observed, and the cationic charge of the products enables the resins to act as an anionic trash catcher.
In tissue applications such dosages are also not sufficient to reach wet strength, but do improve the creping process of the paper web on the yankee cylinder.
Dosages from 1 to 2 % (as it is) reinforce the surface strength required in printing, but also support the runnability of LWC in production lines with online-coaters.
Label and security papers (bank notes) require very high wet strength properties, which do request product dosages up to 10 % (product as it is based on dry fibers)
Opposite to formaldehyde resins, which show best performance under acidic conditions, the epichlorohydrin resins perform best under neutral pH conditions, which meets the demands of modern paper making with the use of calcium carbonate and recycled fibers.
Fig. 2 shows the performance of different products, measured as wet breaking length of the paper sheet with the same dosage (dry product based on dry fibers) as a function of the pH-value.
Formaldehyde resins cannot be recommended at all in systems with a pH above 6, while epichlorohydrin resins may be preferentially used between 5 and 8.

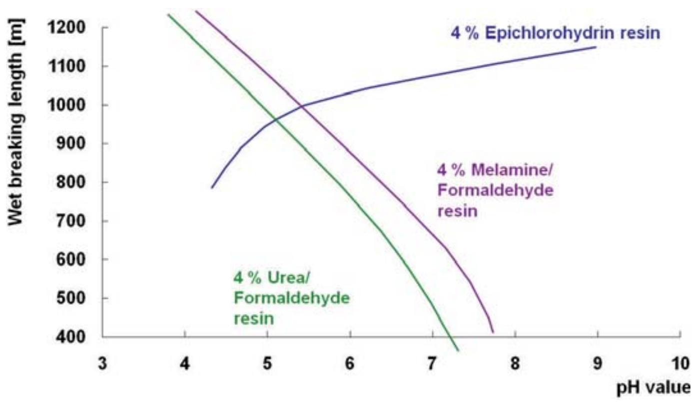

Fig. 2: pH application range of wet strength resins

In production scale pH-values above 8 should be avoided, since the epichlorohydrin resins start to hydrolyze and elongated contact times with such pH will result in a serious performance drop.

2. Chemistry of Polyamidoamine-epichlorohydrin based wet strength resins

Polyamidoamine-epichlorohydrin resins are produced in a 2-pot synthesis *(Fig. 3).* In the first step a pre-condensate is manufactured. In

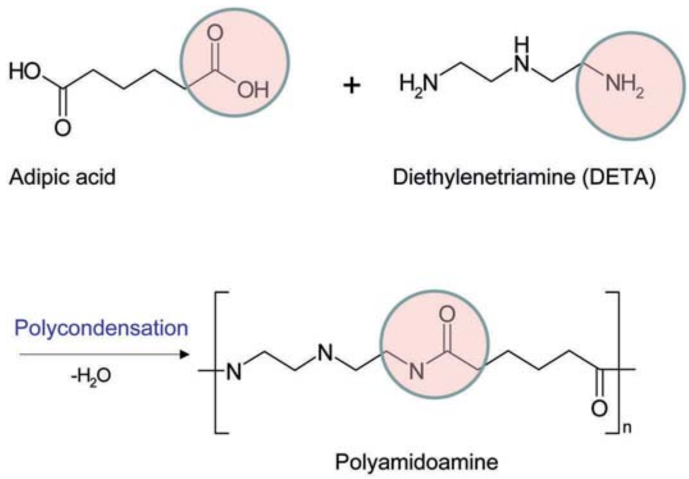

Fig. 3: Manufacturing of the Pre-Polycondensate

this step a bifunctional carboxylic acid, for instance adipic acid, is heated up together with bifunctional amines like ethylenediamine and /or diethylenetriamine and/or other multifunctional primary or secondary amines. Water is removed continuously to push the condensation reaction. The result is a linear or cross-linked polyamidoamine. The ratio of the monomers, the ratio amide to amine and the molecular weight are major parameters of this synthesis step.

The pre-condensate shown in the previous Fig. does not have tertiary or quaternary amine groups. Hence, only slight cationic charge can be measured. Adsorption on cellulose cannot be expected. Furthermore, the precondensate has no functional groups to perform cross-linking reactions, which are essential to achieve wet strength in paper.

In a second reaction the pre-condensate is converted with epichlorohydrin to form reactive intermediates shown in *Fig. 4.* In a first step, an aminochlorohydrin is formed, which may react to the azetidinium salt shown at the bottom of this slide. This explains the rise in cationic charge in the polymer and the reactivity of the polymer (as a consequence of ring-tension of the azetidinium group).

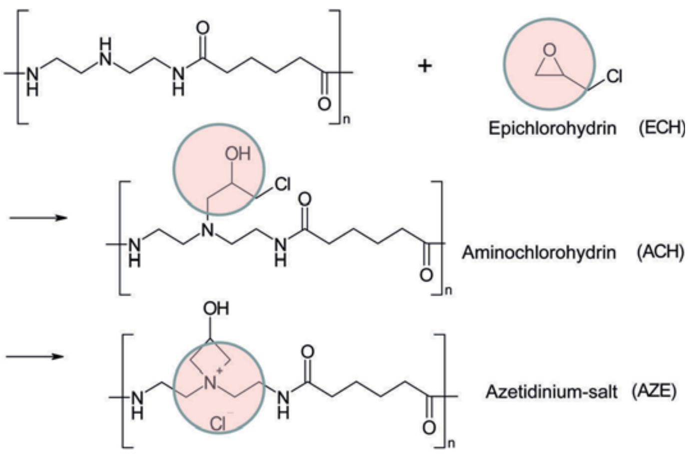

Fig. 4: Activation with epichlorohydrin

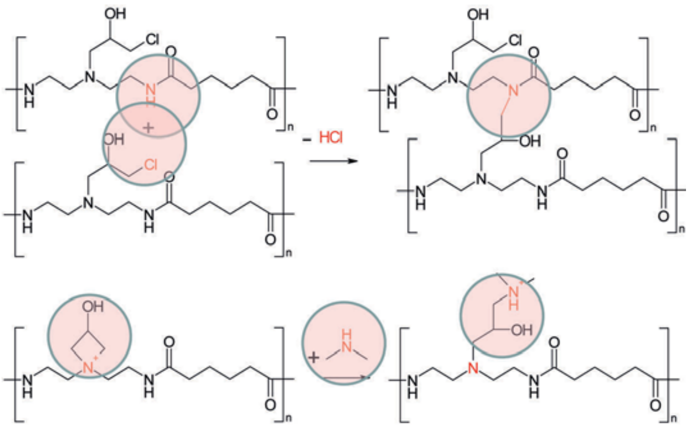

Fig. 5: Crosslinking reactions

The intermediates shown in *Fig. 5* are subject to further conversions during storage, resulting in cross-linking of the poly-condensate. This can be measured in terms of viscosity. The product stability (shelf life) depends on accurate adjustment of the pH. Acidic conditions stabilise the intermediates, but alkaline pH-values generate hydrolysis reactions and decomposition of the poly-condensate.

Further cross-linking of the epichlorohydrin resin, which has been adsorbed on the fibers, happens in the drying section of the paper machine. 90 % of the resin is adsorbed immediately after the addition to the paper stock. Parts of the product remaining in the white water belong to a low molecular weight fraction, have less cationic charge and are higher in organic chlorine content compared to the original product before dosage to the pulp furnish.

Two different mechanisms are discussed during curing of the resin on the fibers: a) reaction of the azetidinium group with secondary amine (homo-cross-linking) and b) reaction of the azetidinium group with cellulose-OH (co-cross-linking) *(Fig. 6).* The first mechanism describes the formation of a polymer network entrapping the fibre-fibre touch-points. The second mechanism describes the formation of covalent cellulose-resin bonds. Most likely both mechanisms happen in reality.

Papermakers expect sufficient shelf life of the wet strength resin but quick and complete curing of the resin in the drying section or soon after production.

Synthesis of epichlorohydrin resins is a chemistry based on organically bonded chlorine. The reactive group needed for the curing of the wet strength resin, the azetinium group, does not contain chlorine any

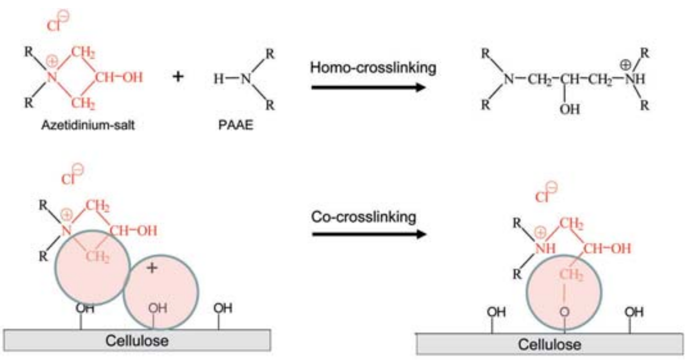

Fig. 6: Homo- & co-crosslinking during paper curing

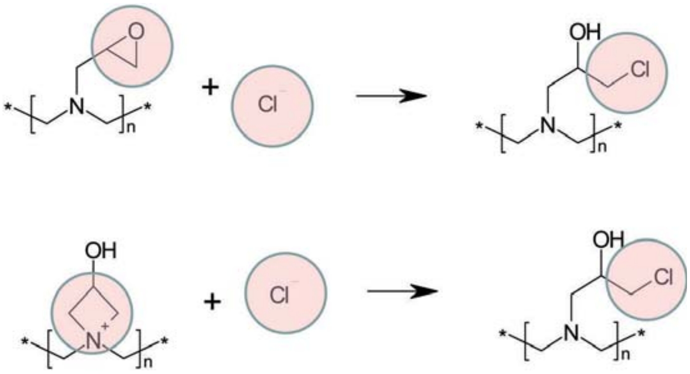

Fig. 7: Re-formation of organically bonded chlorine

more, but, as shown in *Fig. 7*, organic chlorine may be formed again by reaction with excessive chloride. Removal of chloride immediately after the product synthesis by means of ion exchange or ultra-filtration is therefore an effective way to suppress the re-formation and to achieve products with ultra-low organic chlorine content. However, to save the costs of such additional procedure, a lot of research has been carried out in the last years to reduce the content of organically bonded chlorine by developments in the chemical synthesis.

Monomeric by-products are formed during synthesis and storage as well, some of those containing organic bonded chlorine, as shown in *Fig. 8*. Dichloropropanol (DCP) and monochloropropandiol (MCPD) are regarded as hazardous substances. Up to now their formation cannot be avoided, but parameters of the synthesis can be chosen to keep the concentration below the legislative limits.

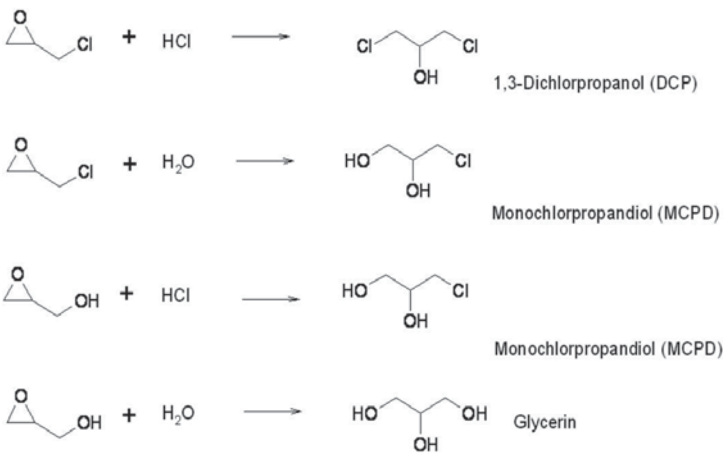

Fig. 8: Formation of by-products during storage and application

A summarizing parameter for the content of total organic bonded chlorine is the AOX. Originally developed to characterize effluents, AOX is nowadays also used to determine the organic bonded chlorine of products, for instance.

AOX, which actually means adsorbable organic halides, is based on the fact, that such halides can be adsorbed almost complete on charcoal. The treated charcoal is then flushed with nitrate solution to remove chloride and is burned afterwards to turn organic halides into their salts (chlorides) which may be determined afterwards by means of ion chromatography or chloride sensitive titration.

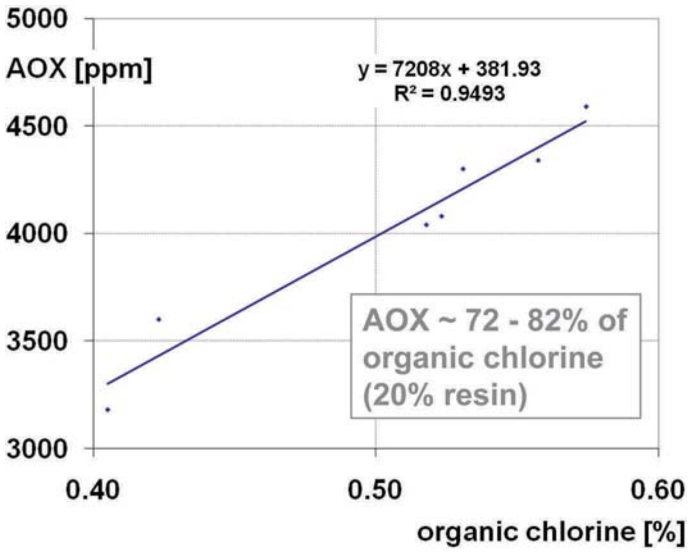

Fig. 9: AOX = f (organic chlorine)

Fig. 9 shows for the case of epichlorohydrin resins, that organic chlorine of these products may be determined via AOX measurement. However, the method does not regain 100 % of the organic chlorine. In particular, low molecular weight substances do not absorb on the charcoal by 100 %.

As mentioned above, organic chlorine may be formed again during storage of the products by reaction of the functional reactive groups

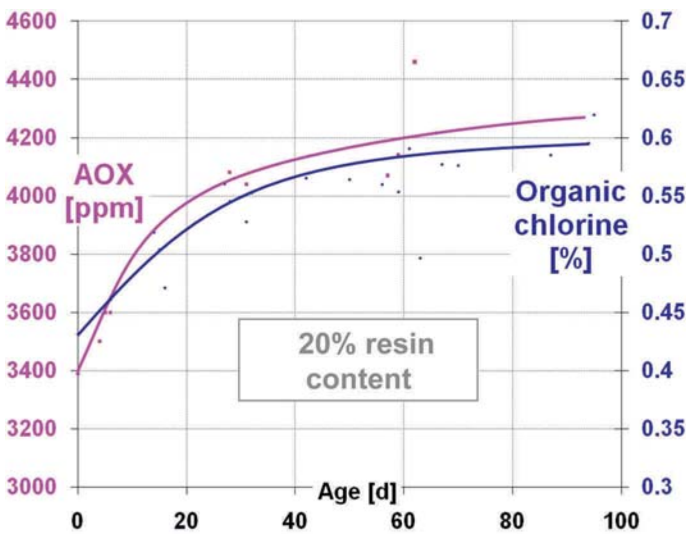

Fig. 10: Re-formation of organic bonded chlorine; AOX and organic chlorine = f (age of product)

with excessive chloride. Hence, it is not recommendable to adjust the pH of these resins with hydrochloric acid. The re-formation of organic chlorine starts immediately after the synthesis of the product and slows down with the consumption of inorganic chloride. *Fig. 10* shows this reaction at the case of a particular epichlorohydrin resin with 20 % dry content.

3. Legislative rules for hazardous by-products in epichlorohydrine resins

Both DCP and MCPD have been classified by the Scientific Committee On Food (SCF) of the European Union, 30.05.2001:

DCP:1,3-Dichlorpropane-2-ol	Classification: genotoxic, carcinogen
MCPD:3-Monochloro-1,2-propanediol	Classification: carcinogen, not genotoxic

Classification is based on studies of the UK Drinking Water Inspectorate from year 2000.
UK COM (Committee on Mutagenicity), October 2000: Studies on bone marrow cells and rat liver proof that MCPD is not genotoxic.
UK COC (Committee on Carcinogenicity), December 2000: NOEL (no observed effect level) of MCPD is being evaluated at 1,1 mg/kg bw/d for creation of cancer in rats.
MCPD is a natural component in food stuff like soja sauce or hydrolyzed vegetable protein with an amount of approx. 1 mg/kg.
Based on recent data SCF decided to introduce a TDI (Tolerable Daily Intake):

NOEL:	1.1 mg/kg bw/d	from the study of UK COC December 2000
Risk factor:	500	due to limited statistically firmed data and other limitations (insufficient reproducibility, ongoing toxicity studies)
TDI:	2 µg/kg bw/d	

With an estimated risk factor of 500, the total daily intake (TDI) for MCPD has been fixed to 2 ug/kg bodyweight/day. This has an impact on the production of food packaging paper and tissue, which needs to be wet-strengthened.
Suppliers of the chemical additive and paper producers as a team need to calculate and make sure that limits of DCP and MCPD in the paper can be undercut continuously.
As an outcome of the calculations for food packaging papers the German legislation has classified Polyamidoamine-epichlorohydrin wet strength resins as follows:

- Products with < 0.1 % DCP are not classified as hazardous goods
- WGK 1 (low water hazard risk)
- Approval according BfR XXXVI (for use in food packaging paper), if DCP < 2 ppb and
  MCPD < 12 ppb
  in the aqueous paper extract

However, with modern wet strength agents based on epichlorohydrin resins, this limits can safely be undercut within the common range of product dosage.
Recently the European Community launched new criteria for the Eco-labeling of Tissue Paper (Commission Decision 2009/568/EC). These criteria describe in detail which raw materials are allowed to be used and which requirements these raw materials need to fulfill. These criteria for wet strength resins are:
….Wet strength aids must not contain more than 0.7 % of the chloro-organic substances epichlorohydrine (ECH), 1,3- dichloro-2-propanol (DCP) and 3-monochloro-1,2-propanediol (MCPD), calculated as the sum of the three components and related to the dry content of the wet strength agent.…
Again, most of the established suppliers of these chemical additives are able to meet the requirements and have suitable products in their offering.
Epichlorohydrin resins have been introduced as wet strength resins into the paper production in the late 1950's. In the 1980's, discussion on chloro-organic compounds in the effluent came up, mainly driven by the pulp bleaching process, but beyond that wet strength resins and some dyes and biocides were regarded as AOX-sources in the effluent, as well.
From 1985 the industry developed new products aiming seriously less AOX, which have been introduced in the market as "2nd Generation". In the 1990's, monomeric by-products, in particular DCP and MCPD, came into focus as they were recognized as hazardous substances. Further product development to comply the limits set by the authorities, for instance for the content of said monomers in food packaging papers, resulted in new products of the 2.5th Generation (by means of variation in the chemical synthesis) and 3rd Generation (by means of cleaning procedures).

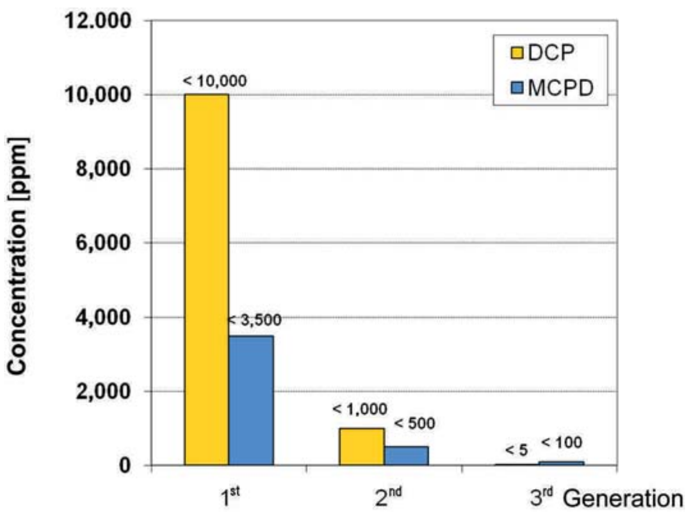

Fig. 11: Reduction of chloro-organic by-products

Fig. 11 gives an overview on the content of DCP and MCPD as typical values for products of the different "Generations".
It can easily be recognised, that impressive success has been achieved by research work in the last 20 years.

4. Mill studies targeting improved environmental goals

What does this mean in real case of a tissue machine? *Fig. 12* shows the results of AOX-measurements in the effluent during a couple of trials on the same machine.
A basic AOX value can be determined even without any wet strength agent. This charge most likely comes from the fiber raws or perhaps from biocides with organic halides.

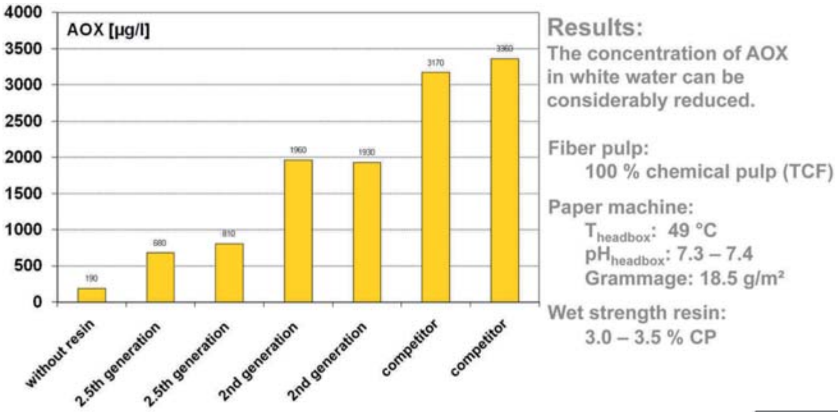

Fig 12: Reduction of AOX in the effluent; Mill study 1 Tissue – Yankee machine

Wet strength resins contribute significantly to the AOX charge, but new developments like the resins of the 2,5th generation do have a seriously lower impact on the whole AOX charge . At least regulatory thresholds can clearly be undercut using those products.

Recently new trials have been started on a Through-Air-Drying machine. Production parameters were:

Fibre pulp: 70 % pine /30 % eucalyptus fibers

Paper machine:

– Production: 70,000 tons/year
– Machine width: 5.3 m
– Grammage: 18 g/m²
– $T_{headbox}$: 44 °C
–$pH_{headbox}$: 7.8–8.0

Wet strength resin: 4–6,5 % CP (commercial product)

In *Fig. 13,* first results are shown of the AOX measurements during this trial. Although the previous product is a wet strength resin of the 2.5th

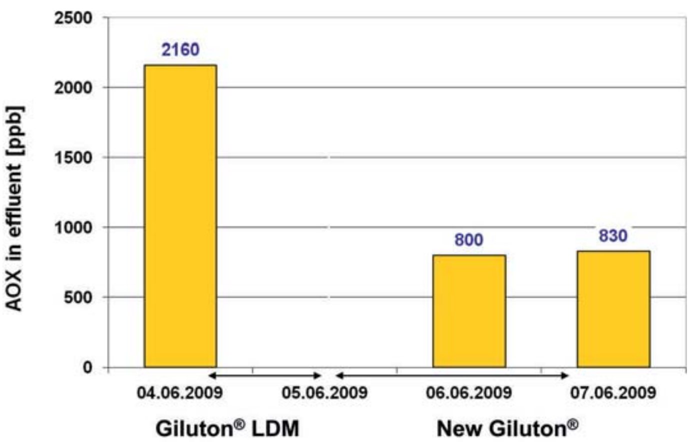

Fig. 13: Reduction of AOX in the effluent; Mill study 2 Tissue – TAD Machine

generation, already, the AOX displayed here with more than 2.000 µg/l could be considered as unusually high. This is due to the technology of this machine, which is equipped with Through-Air-Drying and hence requests significantly higher wet strength dosages compared to a conventional Yankee cylinder.

The trial with the new product at comparable dosages resulted in significantly lower AOX charges. In between, a lot more measurements have been carried out and it has been proven that values down to 700, which is 1/3 of the previous situation can be reached.

Fig. 14 points out that the performance of the new product could be kept almost at the same level. The box in the corner right above compares AOX and chloro-organic momomer content of both products. AOX in the product could be reduced significantly, while MCPD as a by-product formed during storage is still on the same level. Anyhow tissue produced with these products do undercut the regulatory limits for DCP and MCPD.

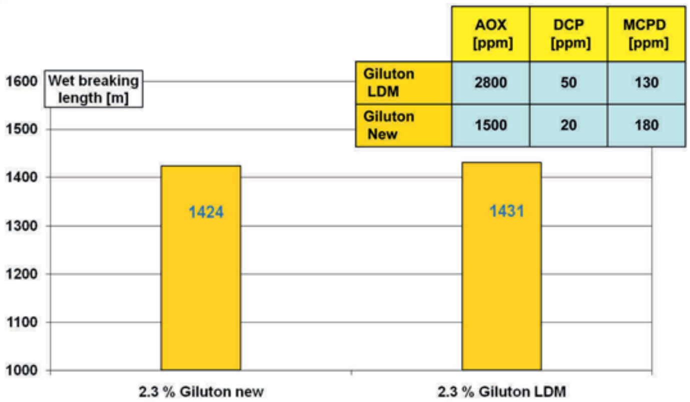

Fig. 14: Impact on wet strength; Mill study 2 Tissue – Pilot scale pre-trial

Not only DCP and MCPD in the paper (which are limited for food packaging paper) but also OX in general is coming into consideration as a criterion to be regarded for food packaging paper and tissue. *Fig. 15* shows that during the first trial with the new wet strength agent

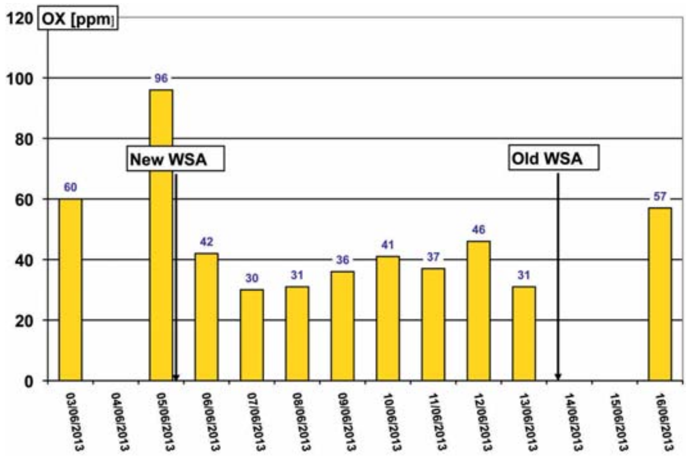

Fig. 15: Reduction of OX in the paper; Mill study 2 Tissue – TAD Machine

also this parameter could be significantly reduced. During the data collection for this presentation, only a lttle evidence was available for the situation before the trial. Meanwhile, enough measurements have been carried out to prove that a reduction of the OX in the paper from 80 ppm down to 40 ppm could be reached. Further steps and new trials for even lower values below 30 ppm are planned already.

Acknowledgement

We are grateful for the discussions with papermakers who carried out the trials described here with us. We learned a lot and would never have succeeded without their contributions.